

# Field and Laboratory Validation of a Portable Subcritical Water Extraction System for Astrobiology Investigations

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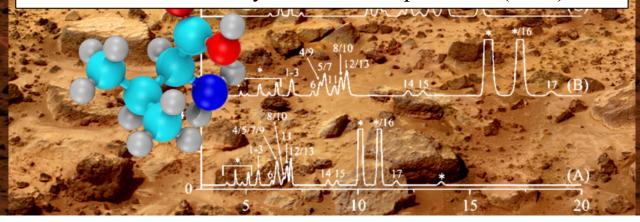




### Overview & Motivation



"... the influence of the mineral matrix and chemical composition on organic compound derivatization, [..], will likely be a major constraint in the ability for SAM to detect amino acids and carboxylic acids." Stalport et al. (2012)



- The search for signs of life beyond Earth.
- Perform chemical analyses on planetary samples to characterize any organic molecules present.
- Interesting targets:
  - Amino acids
  - Carboxylic acids
- GC-MS:
  - High TRL and ideal for volatile species
  - Limitations for non-volatile organics
  - Derivatization & pyrolysis



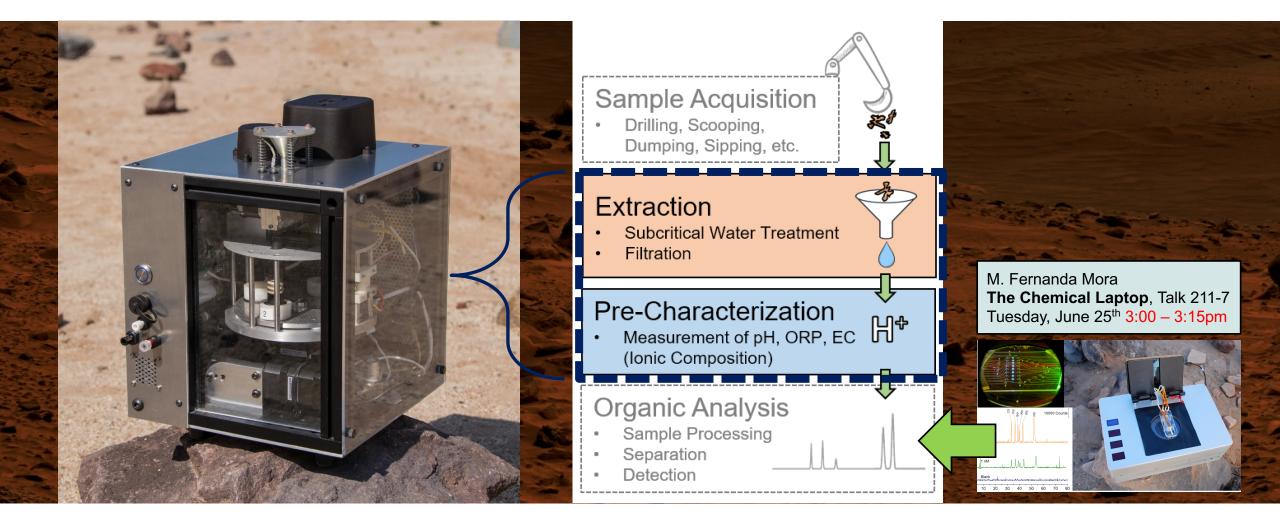
### Overview & Motivation



- Promising way: Liquid-based extraction!
- Previous Systems:
  - Low TRL
  - Manually operated
  - Not validated in a relevant end-toend scenario
- Here we present first automated and remotely operated SCWE, validated on test rover in Atacama Desert.



### ALEXIA: Automated Liquid Extractor for In-Situ Astrobiology



Kehl et al. (2019) Patent pending.

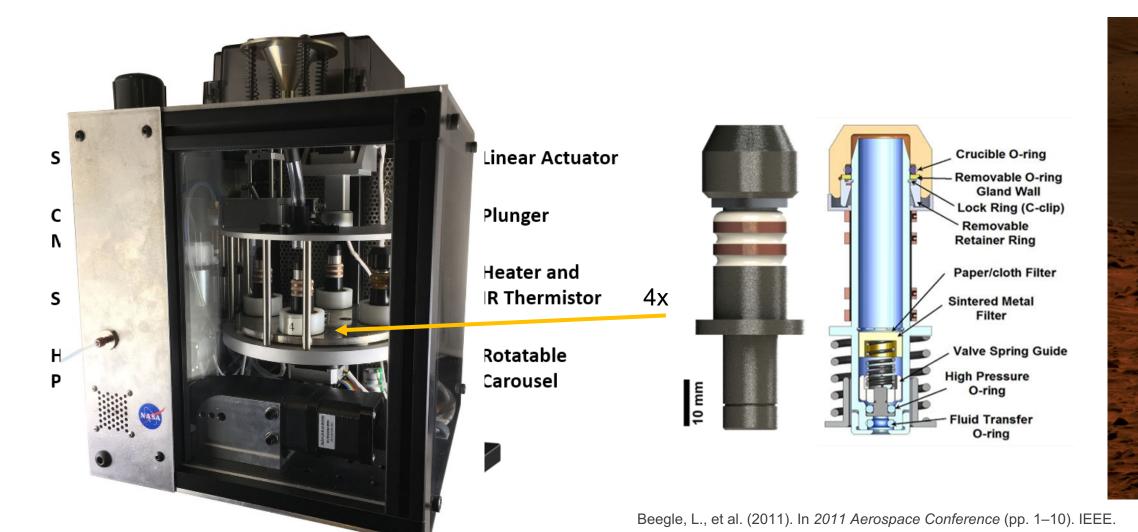


- Extraction principle: Water is superheated and pressurized to keep it from boiling.
- Liquid water greatly varies its dielectric constant as a function of temperature and pressure.
- Cells are lysed, proteins are hydrolyzed into peptides and amino acids, and bound molecules can be cleaved from mineral matrix
- Efficient extraction of a variety of organic compounds using a single, nontoxic, and environmentally benign solvent: water.



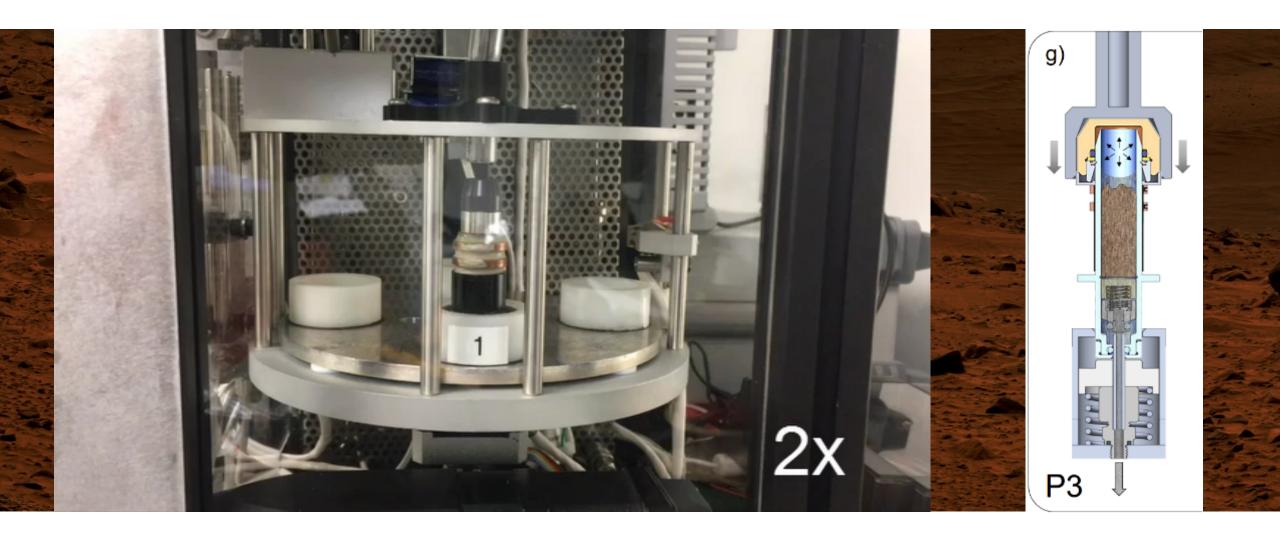


### **ALEXIA: Core & Extraction Cells**



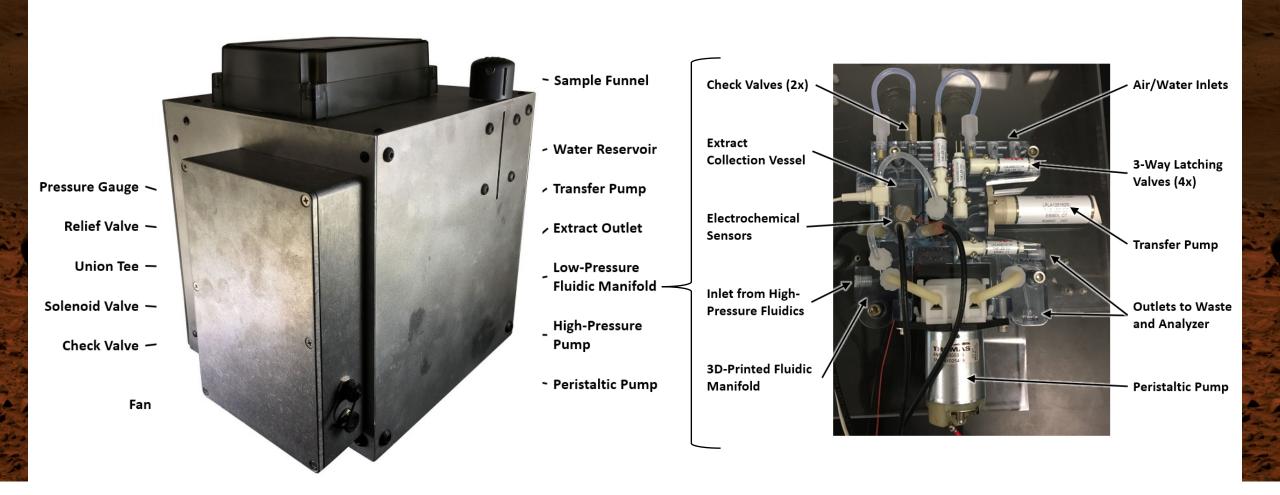


### **Extraction Procedure**



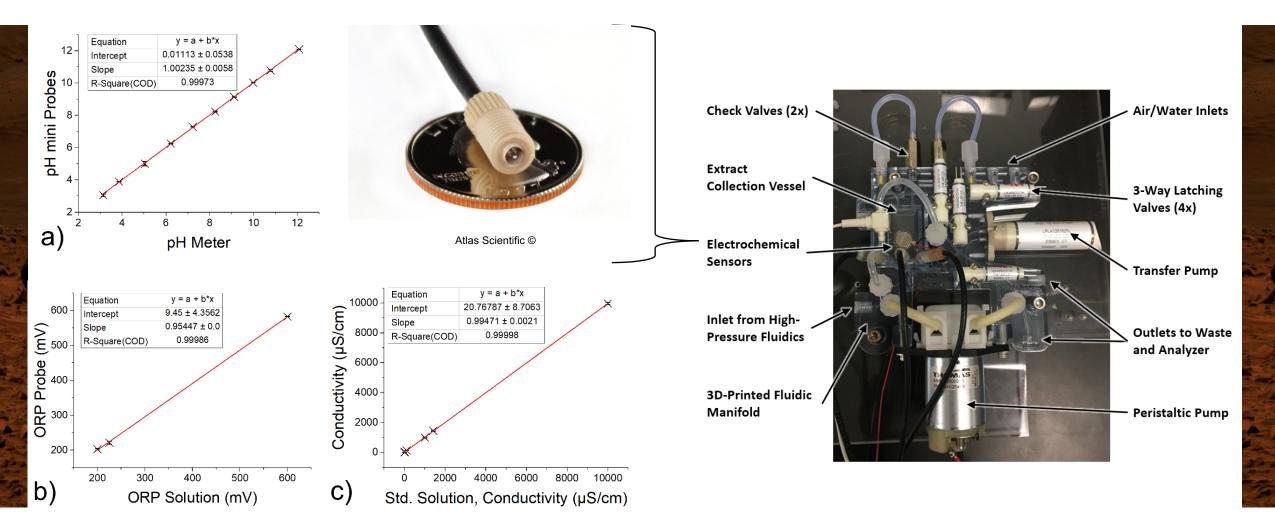


### Low-Pressure Fluidics & Pre-characterization





### Internal Electrochemical Sensors



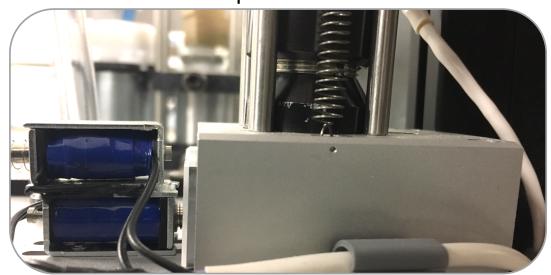
### System Features & Telemetry



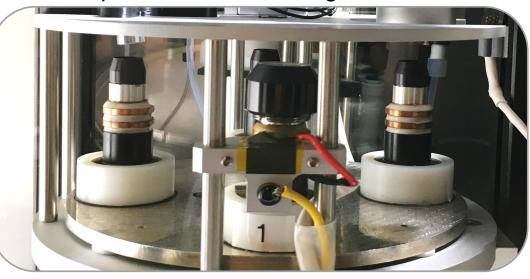
Vibrating Funnel & Sample Portioner



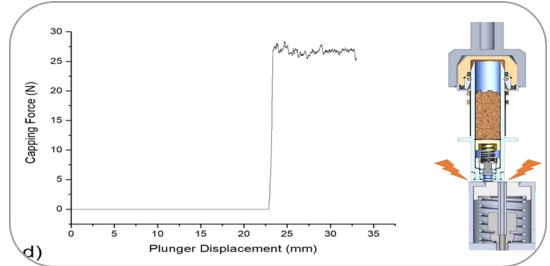
Automated Cap Release Mechanism



Sample Carousel with Magnetic Encoder



Sealing Mechanism with Force Sensor

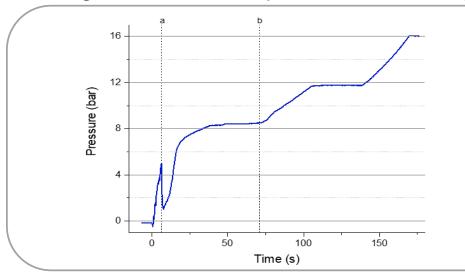


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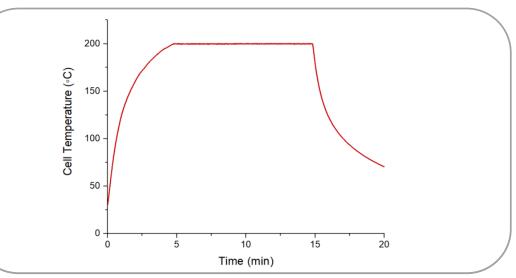
# System Features & Telemetry



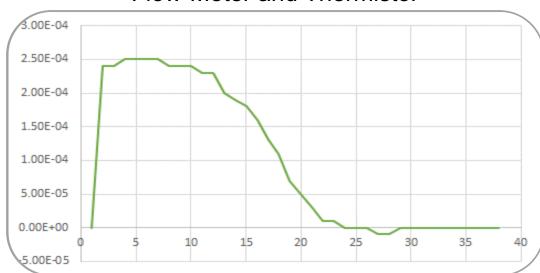




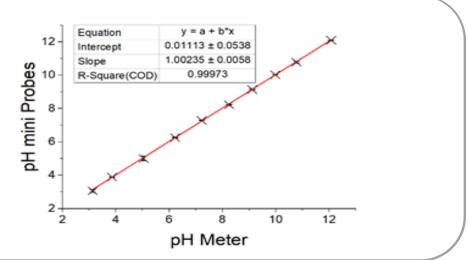
Internal Heater & Contactless IR Thermistor



Flow-Meter and Thermistor



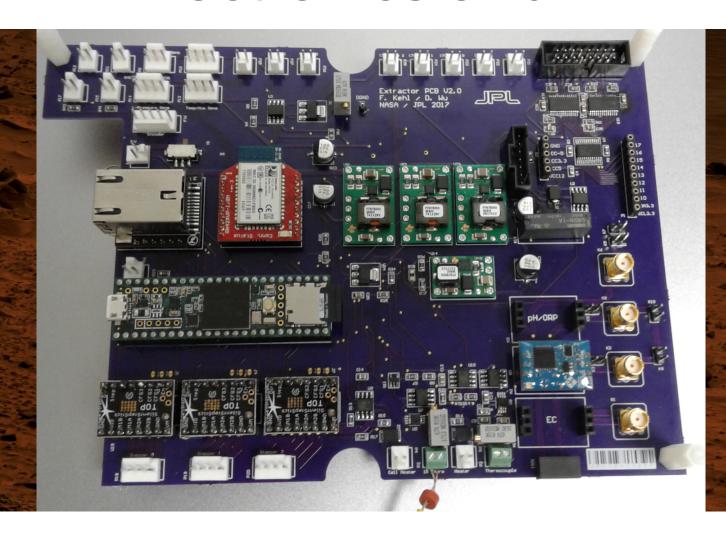
Miniaturized pH, ORP and EC Sensors



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### Electronics and Firmware



#### Specs:

- 32 bit 180 MHz ARM Cortex-M4
- SPI, I<sup>2</sup>C, UART, RS-485
- Ethernet & wireless communication
- 50 W heater & IR thermistor circuitry
- Pressure gauge and flow sensor
- Control 12 valves and 3 pumps
- 3 stepper motor controllers
- Electrochemical sensing fro preanalysis of extract



### Graphical User Interface

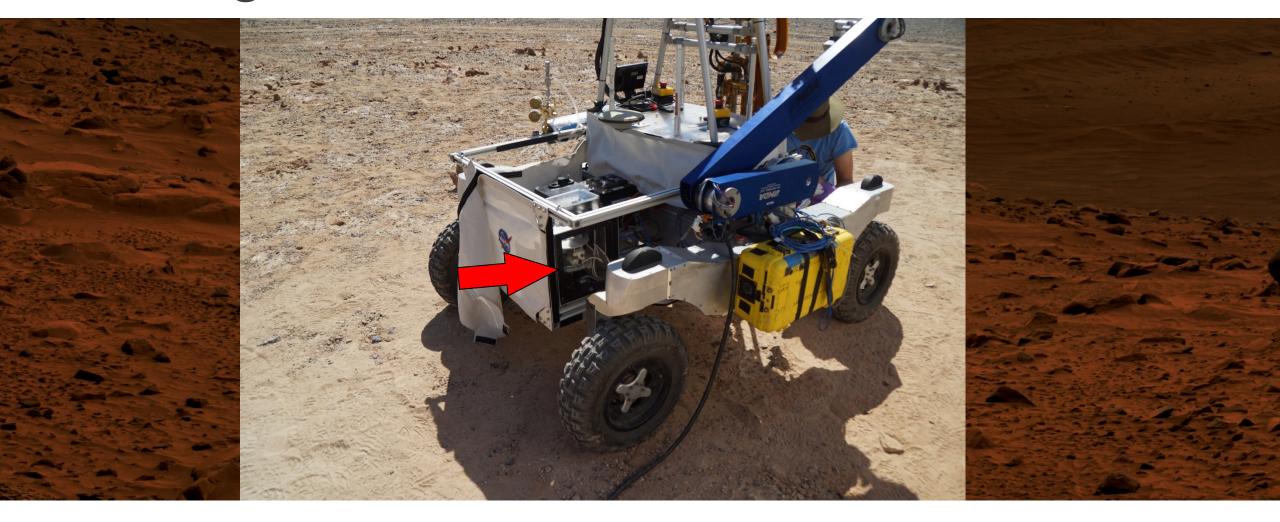








# Integration on KREX2 Rover



# Remote operation testing of California Institute of Technology extractor on remotely operated rover



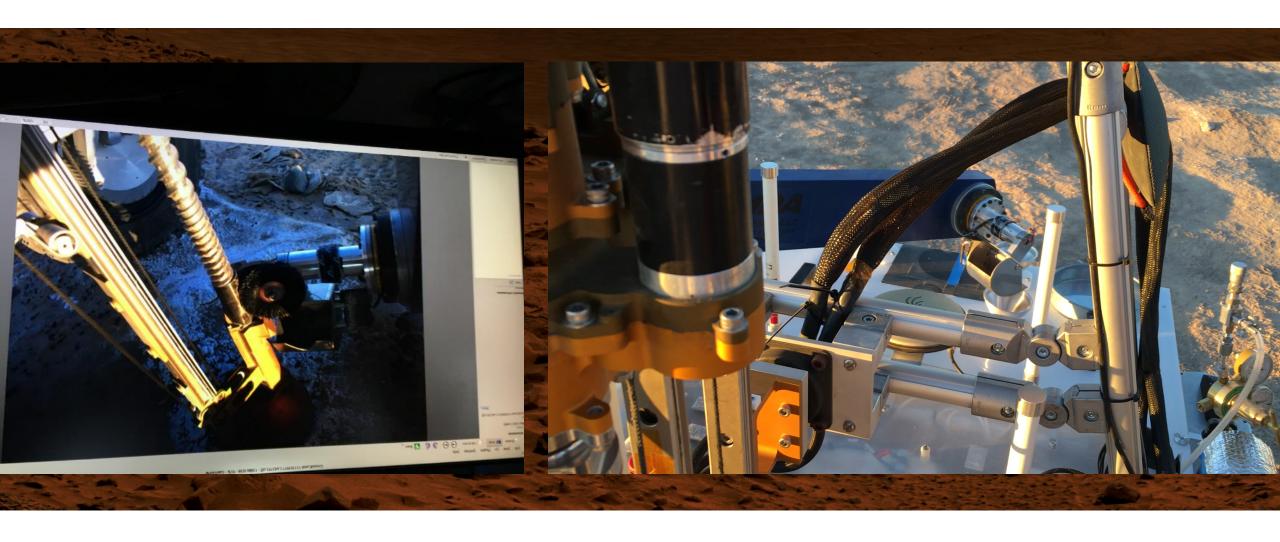


# Remote Operations/Comms



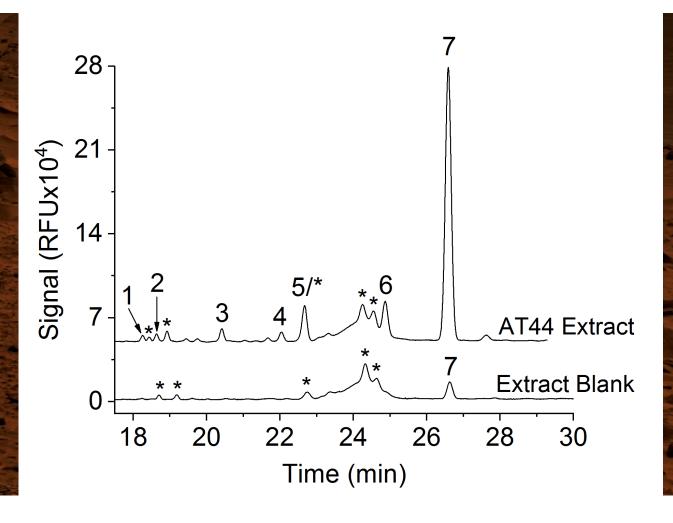
# Automated sample acquisition with drill and robotic arm







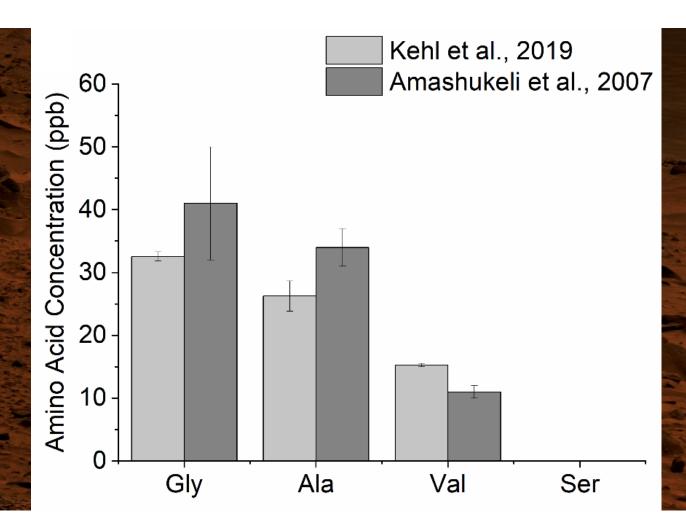
# Amino Acid Analysis by CE-LIF



- Soil samples were brought back to JPL for extraction and analysis by capillary electrophoresis coupled to laser-induced fluorescence (CE-LIF).
- 185 °C for 45 min
- 12 to 217 nM
- SCWE required: no amino acids extracted at room temperature.



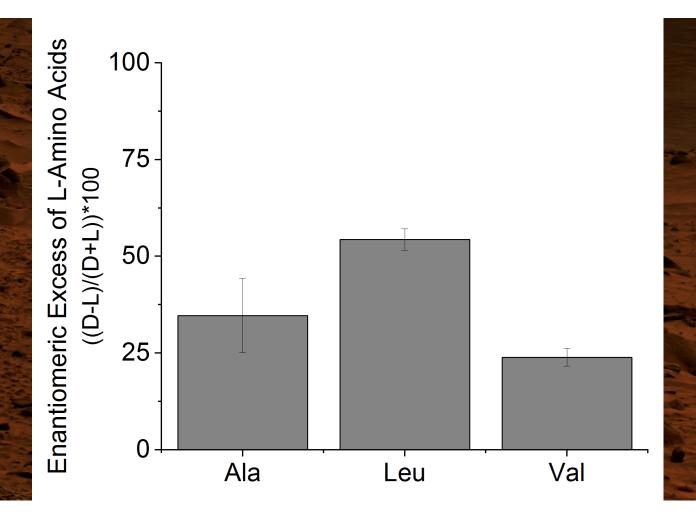
### Total Amino Acid Abundance



- Total amino acid abundance extracted at 185 °C for 45 min is comparable to what Amashukeli et al. reported in 2007 (200 °C for 30 min).
- No serine, as it degrades quickly at high temperatures
- More work needed to increase extraction efficiency



### **Enantiomeric Excess of Chiral AAs**



- Obtaining chiral information about amino acids is a key scientific benefits of using CE-LIF.
- Enantiomeric excess is a powerful indicator for biotic origin of AAs.
- Excess of the L-form, as expected for samples containing terrestrial life.



### Electrochemical Analysis

Extract	ORP (mv)	рН	EC (µS/cm)
Blank (185 °C, 45 min)	313 ± 2	7.45 ± 0.05	130 ± 10
Cold (25 °C, 45 min)	311 ± 1	6.67 ± 0.05	1410 ± 10
Hot (185 °C, 45 min)	303 ± 2	7.50 ± 0.05	160 ± 10

- Analyzed ORP, pH and EC of blank, cold and hot (same sample) extract.
- ORP and pH remained almost the same, the electrical conductivity increased by an order of magnitude.
- Room temperature water can effectively remove salts contained in the sample.



### Summary & Outlook



- Liquid extraction is an enabling technique to measure
   AA and CA at PPB levels, e.g. by CE-LIF.
- Demonstrated first remotely controlled end-to-end or "dirt-to-data" SCWE on a rover in the Atacama Desert.
- Characterized the extract with electrochemical sensors.
- Demonstrated extraction and subsequent chiral analysis of AA at nM concentrations. We found life!
- Outlook: Return to Atacama Desert this fall and connect it to Chemical Laptop for end-to-end organic analysis. (see, The Chemical Laptop, Talk 211-7, M. Fernanda Mora, Today 3:00 3:15pm)

### Acknowledgements

Konstantin Zamuruyev Peter Willis Nathan Oborny Portable CESI-MS System CE Analysis for Europa **Radiation Tolerant Hardware** Poster 139-143 Talk 408-3 Poster 139-146 Monday, June 24th Thursday, June 27th Monday, June 24th 5:00 - 7:00pm2:00 - 2:15pm5:00 - 7:00pm**Aaron Noell MICA** Talk 408-7 Thursday, June 27th 3:00 - 3:15pmElizabeth Jaramillo CE-C4D of lons Jessica Creamer Talk 103-7 Chiral Amino Acid Analysis Monday, June 24th Talk 107-3 11:45am - 12:00pm Monday, June 24th 2:00 - 2:15pm

- Funding from NASA/JPL programs: PICASSO, PSTAR, NPP/USRA
  - Peter Willis and entire Chemical
    Analysis and Life Detection Group
- Ball Aerospace, Luther Beagle,
   David Wu, Eric Tavares Da Costa,
   Kevin Lee

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M. Fernanda Mora The Chemical Laptop Talk 211-7 Tuesday, June 25<sup>th</sup> 3:00 – 3:15pm

Jet Propulsion Laboratory
California Institute of Technology



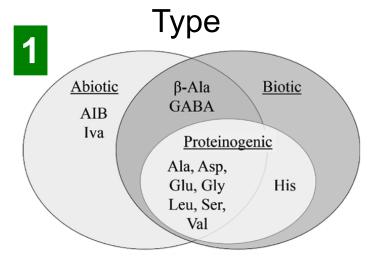
jpl.nasa.gov

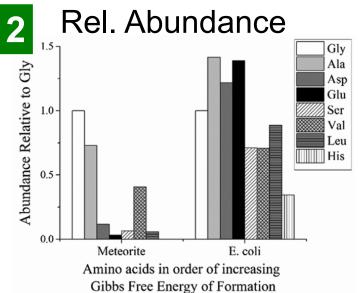


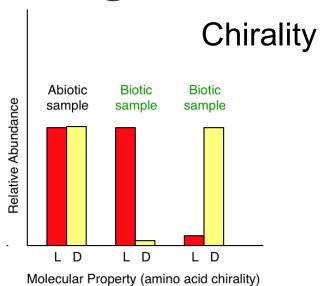
# Backup Slides

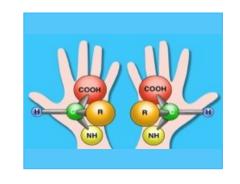


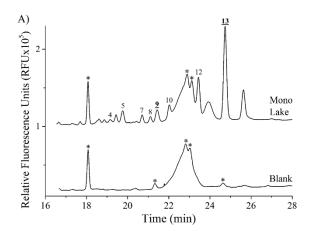
### Amino Acids as Biosignatures













Creamer, J. S., et al. (2017). *Analytical Chemistry*, 89(2), 1329–1337. Willis, P. A., et al. (2015). *Analytical and Bioanalytical Chemistry*, 407(23), 6939–6963.



- Water is superheated and pressurized to keep it from boiling.
- Permittivity, viscosity, ionization constant and surface tension of water are decreased.
- Diffusion rate increased.
- The process dissolves organics and hydrolyzes proteins.
- We perform SCWE at < 250C to prevent thermal degradation of amino acids.

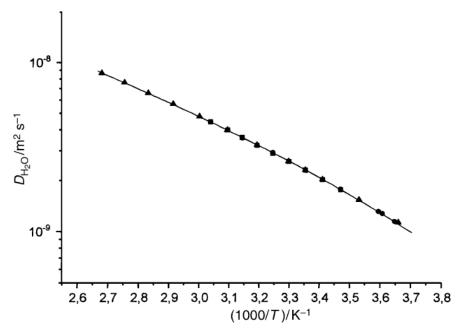


Fig. 1 Arrhenius plot of experimental self-diffusion coefficients for  $H_2O$  from isotopic tracer method  $[(\bullet)$ , ref. 5 and  $(\blacktriangle)$ , ref. 6] and from PFG NMR measurements  $(\blacksquare)$ , this paper. The fit curve represents a Speedy-Angell power-law approach [eqn. (1)] with the parameters given in the text.



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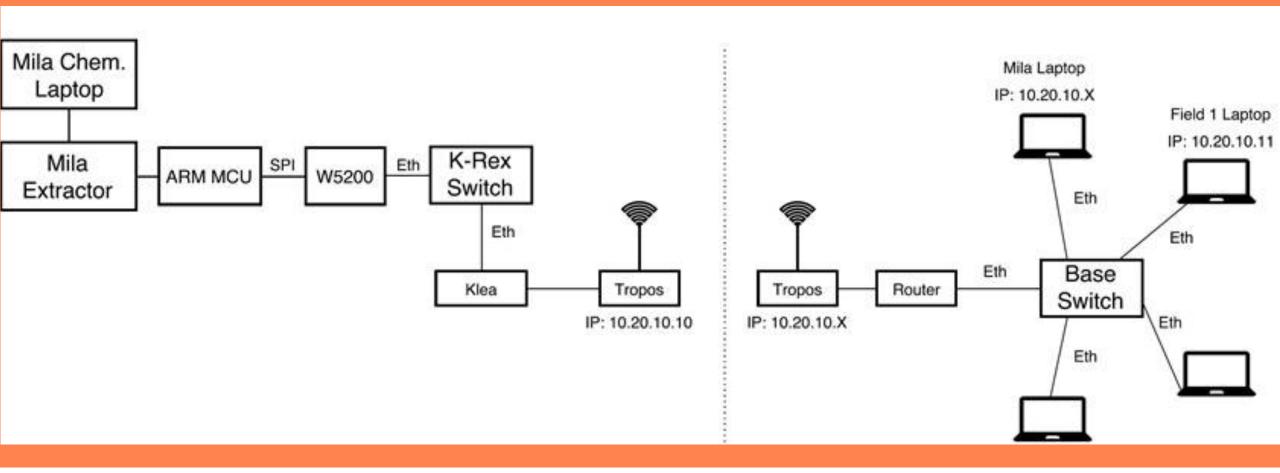


	← Subcritical Water Supercritical Water →												
ε of H <sub>2</sub> O at various T values and 500 bar.	79.5 @ 25 °C	76.0 @ 35 °C	60.6 @ 85 °C	46.4 @ 145 °C	38.8 @ 185°C	32.5 @ 225 °C	25.7 @ 275 °C	19.9 @ 325 °C	14.5 @ 375 °C	8.9 @ 425 °C	4.4 @ 475 °C	2.8 @ 525°C	2.3 @ 575 °C
ε of organic solvents at 25 °C and 1 bar.	water 79.5			DMSO 47	ACN 37.5	methanol 32.6	ethanol 24.6	acetone 20.7	butanol 15.8	THF 7.6	CCI <sub>4</sub> 4.8	CI- benzene 2.7	benzene 2.3
ε ranges over which different organic molecules are soluble	Carbohydrates(e.g.aldoses,ketones,glycosides,deoxy and amino sugars, glycosides, disaccharides, etc.)  Peptides and amino acids												
	Lipids (e.g. triacylglycerols, fatty acids, phosphoglycerides, sphingolipids, terpenes, steroids, etc.)												
	Heterocycles (e.g. pyrroles, furans, thiophenes, pyridines, pyrimidines, nucleic acids, etc.)												
	PAHs												

Teo, C. C., Tan, S. N., Yong, J. W. H., Hew, C. S., & Ong, E. S. (2010). Pressurized hot water extraction (PHWE). Journal of Chromatography A, 1217(16), 2484–2494 Smith, R. M. (2002). Extractions with superheated water. Journal of Chromatography A, 975(1), 31–46. http://doi.org/10.1016/S0021-9673(02)01225-6 Holz, M., Heil, S. R., & Sacco, A. (2000). Physical Chemistry Chemical Physics, 2(20), 4740–4742



### Successfully set up remote comms





### Crucible Injector Interface

